Soft X-Ray Spectromicroscopy Investigation of Colloid Particles Responsible for Groundwater Actinide Transport

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Introduction: Long-term isolation and immobilization of long-lived radionuclides, mostly actinide elements, is the major goal of nuclear waste repositories in geological formations. To ensure this goal, the impact of colloidal 'carriers' for actinide elements in the geosphere must be understood. Both organic colloids such as humic acids (HA) and inorganic colloids such as hydrous ferric oxides (HFO) or clays can be highly mobile in groundwater aquifers at conditions, which would normally enhance actinide immobilization [1]. Investigations of actinide binding properties of HA implicate COOH groups as the primary functions complexing metal ions [2]. However, the morphology of the colloid sorbent is thought to influence metal affinity as well. Hence, there is a strong necessity for combining morphological studies with chemical, functional group information.

Methods and Materials: We performed soft x-ray spectromicroscopy investigations of aqueous colloid suspensions using the scanning transmission x-ray microscope at NSLS beamline X1A (outboard-STXM). STXM images of HA, HA aggregates formed following addition of Eu(III), chosen as a homologue for trivalent actinides, montmorillonite clay particles, mixed suspensions of clay + HA, clay + carboxylated polystyrene (PS) microspheres, chosen as reference organic colloids, and HFO + HA were recorded. Changes in the *C* 1s NEXAFS upon Eu(III) cation complexation by HA at near-neutral pH were compared to results for a synthetic model HA, M42 [3], which has similar metal binding properties.

Results: HA agglomerates in STXM micrographs appear as both globular and filament-type particles, having only diffuse contours. More defined structures appear in the mixed colloid systems. STXM images of clay + HA show HA to coat the clay surface leading to fractal-like aggregates [4]. *C* 1s NEXAFS spectra extracted from STXM image stacks of the carboxylated PS and HA agglomerates reveal electronic transitions corresponding to functional groups (C_6H_6, C=O) present in HA and the reference colloids. If the HA metal cation complexation is selectively mediated by COOH groups, an influence on the corresponding $1s \rightarrow \pi^*$ transition peak might be expected. However, our initial results indicate segregation of different HA species upon Eu(III)-mediated HA agglomeration. The STXM micrograph of these agglomerates (Fig. 1) reveals darker, dense regions dispersed in lighter, less absorbing regions. The darker regions exhibit *C* 1s NEXAFS similar to that obtained for HA agglomerates at pH 4.4 and a HFO + HA suspension. The spectrum extracted from the lighter regions shows additional absorption features with energies comparable to those observed for aliphatic $-CH_3$ and $-CH_2-$ groups. STXM micrographs of M42 after addition of Eu(III) show only homogeneous agglomerates.

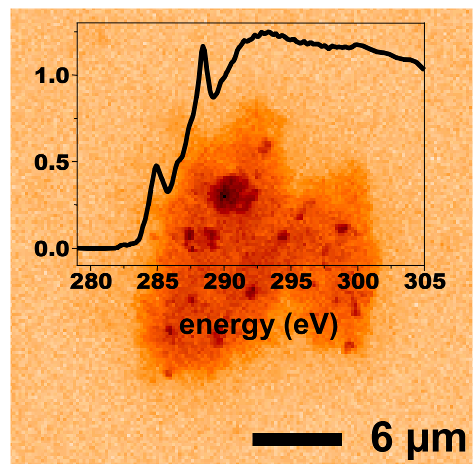

Figure 1. STXM micrograph (288.7 eV) of a humic acid agglomerate following Eu(III) complexation - inset shows *C* 1s NEXAFS obtained from dark regions.

Conclusions: Separation of natural HA into light and dark regions with varying amounts of aliphatic carbon groups induced by Eu(III) may be equivalent to a phase separation into HA fractions with different cation affinities. Eu(III) complexation does not observably effect HA functionality, more its morphology. The uniform agglomerates observed for M42 reflect its greater chemical homogeneity compared to natural HA.

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